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## **Title page**

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## **Evaluating Ligands for use in Polymer Ligand Film (PLF) For Plutonium and Uranium Extraction**

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### **Abstract**

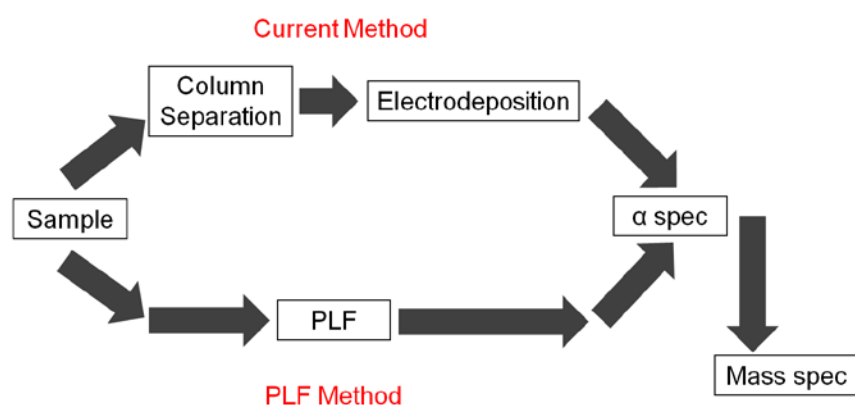
This paper describes a new analyte extraction technique using Polymer Ligand Film (PLF). PLFs were synthesized to perform direct sorption of analytes onto its surface for direct counting using alpha spectroscopy. The main focus of the new technique is to shorten and simplify the procedure for chemically isolating radionuclides for determination through a radiometric technique. 4'(5')-di-t-butylcyclohexano 18-crown-6 (DtBuCH<sub>18</sub>C<sub>6</sub>) and 2-ethylhexylphosphonic acid (HEH[EHP]) were examined for plutonium extraction. Di(2-ethyl hexyl) phosphoric acid (HDEHP) were examined for plutonium and uranium extraction. DtBuCH<sub>18</sub>C<sub>6</sub> and HEH[EHP] were not effective in plutonium extraction. HDEHP PLFs were effective for plutonium but not for uranium.

### **Keywords**

PLF, Thin film extraction, HEH[EHP], HDEHP, crown-ether, actinide

### **Introduction**

A thin film extraction method had been utilized by several authors to selectively extract analytes from a liquid medium [1–8]. This technique is similar to resin based extraction, where ligands are coated or fixed to polymer to separate analytes from the solution. The main benefit of this technique is that the thin film surface provides an easier path forward for radiometric analysis for the alpha emitting nuclides. With this technique, typically two-step process of column separation and electrodeposition can be combined into a single step, which greatly reduces the overall analysis time. The difference between two methods are illustrated in Fig. 1.



**Fig. 1** Diagram comparing conventional sample preparation method and PLF method

Surbeck has reported the possibility of using  $\text{MnO}_2$  thin film to extract radium from a water sample with six-hour exposure time and directly measuring radium with alpha spectroscopy [7]. The resolution of alpha spectra was similar to the energy resolution of a typical electrodeposited source. Surbeck also prepared thin films out of commercially available resin beads to uranium extraction. The films were prepared by fixing finely ground resin beads onto a flat surface. Fifty percent of uranium was recovered within 4 hours, and 80% was extracted in about 20 hours [7]. The alpha spectroscopy energy resolutions were, however, poor in these samples; probably due to the unevenness of the film surface. Wang et al. used a  $54 \text{ mm}^2$  Aliquat-366/PVC liquid membrane system to extract  $\text{Cd(II)}$  from  $\text{HCl}$  solution [9]. The membrane was prepared by dissolving Aliquat-366 and PVC in THF then poured into a mold.

Our research group has demonstrated and reported the possibility of rapid separation of radionuclides using polymer thin film (PLF) [1–3]. Di(2-ethyl hexyl) phosphoric acid

(HDEHP) and bis(2-ethylhexyl) methanediphosphonic acid ( $\text{H}_2\text{DEH}[\text{MDP}]$ ) ligands were both examined for radionuclide extraction in PLF form. HDEHP and  $\text{H}_2\text{DEH}[\text{MDP}]$  based PLF has shown effectiveness in extracting plutonium from nitric acid solution [1–3]. Plutonium and americium were also effectively extracted using  $\text{H}_2\text{DEH}[\text{MDP}]$  based thin polymer film with an extraction time of only two hours [2, 3]. In  $\text{H}_2\text{DEH}[\text{MDP}]$  previous studies, several extraction conditions were examined to find an optimal condition for plutonium and americium extraction. The first experiment indicated strong absorption of plutonium and americium by  $\text{H}_2\text{DEH}[\text{MDP}]$  based PLF in a 0.1 M nitric acid solution [2]. The second study determined that out of several polymers, polystyrene gave the best combination of analyte recovery and alpha spectra resolution [3]. In addition to HDEHP and  $\text{H}_2\text{DEH}[\text{MDP}]$ , our research group has investigated the possible use of HEH[EHP] and  $\text{DtBuCH}_{18}\text{C}_6$  for plutonium extraction. These ligands are commercially available and manufacture information shows high uptake of plutonium and uranium [10]. HEH[EHP] is mainly designed for lanthanide separation; however, due to its similarity to HDEHP, it has great potential to be also effective for plutonium separation in PLF form.  $\text{DtBuCH}_{18}\text{C}_6$  was mainly designed for strontium extraction, but it also showed affinity to plutonium at high nitric concentration. The plutonium extraction capability of PLFs prepared with these two ligands were compared to the one already established from  $\text{H}_2\text{DEH}[\text{MDP}]$  and HDEHP [1–3].

## **Experimental**

PLFs were prepared by incorporating ligands in a polystyrene structure. The stock solution was prepared by dissolving the ligands and polystyrene in Tetrahydrofuran (THF). The films were prepared with a solvent casting method using a 40 mm diameter stainless steel substrate with depth of 2.0 mm. 1 mL of a stock solution was deposited to prepare a thin film. The deposited solution was dried at room temperature for at least 12 hours to evaporate THF and form a solid film. These solidified films weighed about 220 mg after evaporation.

The physical appearance of the PLFs changed depending on the amount of ligand in the film. The polystyrene used in the experiment was clear in its natural form, and the ligand was the only component causing the color change. Typically the films become more opaque with increasing ligand mass. A detailed PLF preparation method had been published in previous works [1–3]. The PLF composition is described as the ratio between ligand and the entire solid mass. For example, PLF with one part ligand and one part polystyrene was assigned 1:2 (wt/wt) ratio.

PLFs were tested over 0.01 to 8M nitric acid solutions for analyte extraction capability.  $^{239}\text{Pu}$  and natural uranium solutions used in this study were prepared in 0.01, 0.1, 1, or 8M nitric acid solution. 2.5 to 3mL tracer solution was directly stippled on the PLF to cover the entire surface with an equilibration time of 3 hours before removing the solution. The tracer solution covered the entire PLF surface initially. However, some of the tracer solution evaporated down to 1 to 2 ml during the equilibration time. After 3 hour equilibration time, solution was removed and PLF was thoroughly rinsed with deionized water to remove any nitric acid left on the surface. PLF was then air dried to remove any water that may have been left on the polymer medium. The plutonium activity of each sample was measured with direct alpha counting to quantify the plutonium recovery by PLF.

### *Materials*

DtBuCH<sub>18</sub>C<sub>6</sub> and HEH[EHP] were obtained from Eichrom Technology Inc. No further purification was done to the ligands. Aqueous solutions were prepared using nitric acid from Fisher Scientific, and ultrapure deionized water was obtained from Barnstead Fi-Stream II Glass Still purification system. Tetrahydrofuran (THF) was obtained from Acros Organics. Polystyrene beads were obtained from Sigma-Aldrich. Polystyrene beads were not cross linked and the average molecular weight was 35,000.  $^{239}\text{Pu}$  and natural uranium tracers were obtained from Eckert & Ziegler Isotope Products Inc.

### *Alpha Spectroscopy*

An Octet Plus system from Ortec, equipped with 900 mm<sup>2</sup> ion implanted silicon detectors, was used in the entire experiment performed in this study. The manufacturer's rated resolution for the detectors was 27 keV FWHM for <sup>241</sup>Am at 5.486 MeV energy. Each detector was for calibrated energy and efficiency using a secondary NIST traceable source. Samples were counted on the top shelf, 4 mm away from the detector surface, for a minimum of 1440 minutes each to measure plutonium activity. The sample holders in the alpha system were modified to accommodate PLF samples by cutting a hole in the middle as shown in Fig. 2. This modification eliminated sample movement during the analysis and increased the consistency in sample analysis condition. The modification ensured consistent sample placement in the vacuum chamber and also provided easier sample handling.

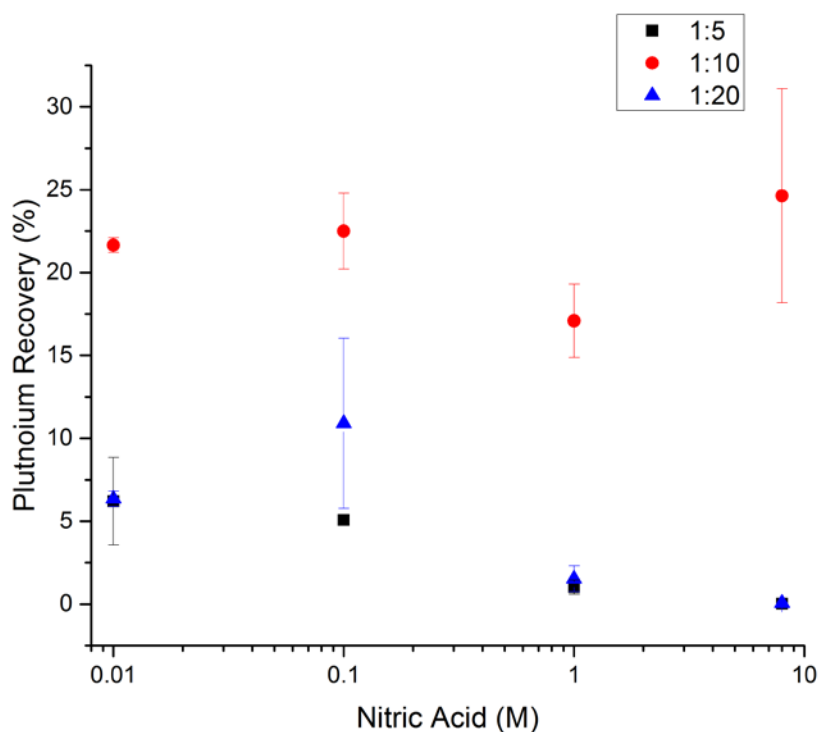


**Fig. 2** Alpha spectroscopy sample tray after modification

## **Results and discussion**

1:2, 1:5, 1:10, and 1:20 HEH[EHP] PLFs were prepared for the study but 1:2 PLF was excluded from the experiment due to its film instability. The large mass of ligand hindered the polymer from solidifying, and ligands were easily washed away from the film structure. The plutonium recovery by HEH[EHP] PLF showed some dependency both on the nitric acid concentration and the composition of the polymer film. Plutonium extraction was most effective with 1:10 PLF in all nitric acid solutions tested in the experiment. The plutonium recoveries by HEH[EHP] PLFs are plotted in Fig. 3. The

plutonium percent recoveries by 1:10 PLF are ranging from 17 to 25%, but these were all within the standard deviation except for the 1M samples. One noticeable plutonium recovery characteristic of HEH[EHP] PLF is that the performance does not decrease at 8M nitric acid. All other ligands examined in previous experiments showed significant decrease in plutonium recovery at 8M nitric acid [1, 11].

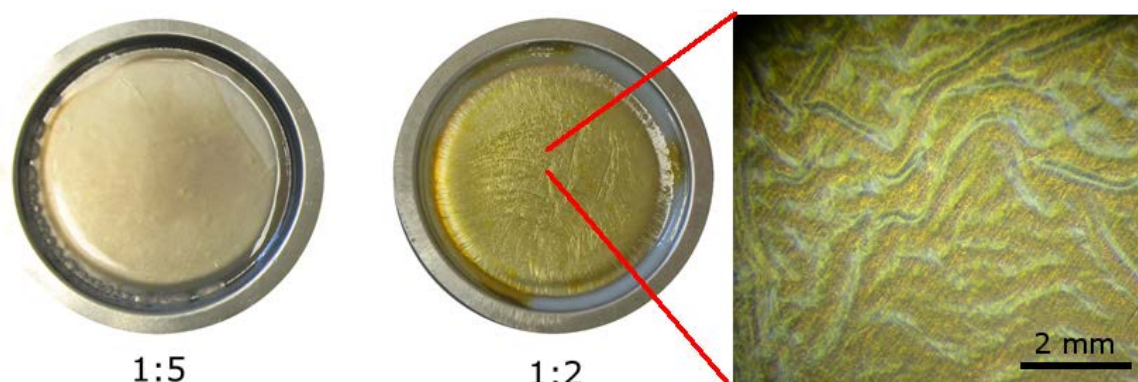


**Fig. 3** Plutonium recoveries by HEH[EHP] PLF in varying nitric acid concentrations

DtBuCH<sub>18</sub>C<sub>6</sub> PLFs were also tested in identical condition as HEH[EHP] PLF. The four different PLFs synthesized with DtBuCH<sub>18</sub>C<sub>6</sub> were all clear and there were no visual differences between them. In the plutonium extraction study, all four DtBuCH<sub>18</sub>C<sub>6</sub> PLFs showed no affinity to plutonium in the entire nitric acid concentration ranges tested. The highest plutonium recovery was observed with 1:20 PLF and 0.1M nitric acid. However, the uncertainty was large and recovery was only around 2.3%. On top of the low plutonium recovery, DtBuCH<sub>18</sub>C<sub>6</sub> PLFs were easily damaged by high concentration nitric acid. The damages caused by 8M nitric acid are more noticeable in 1:2 and 1:5 DtBuCH<sub>18</sub>C<sub>6</sub> PLF. The surface damages caused to 1:2 and 1:5 PLF by 8M nitric acid are shown in Fig 4. Discoloration was observed in both PLFs. Both PLF surfaces were etched by the acid. The degree of etching was greater in 1:2 PLF than 1:5 PLF. It is clear that the



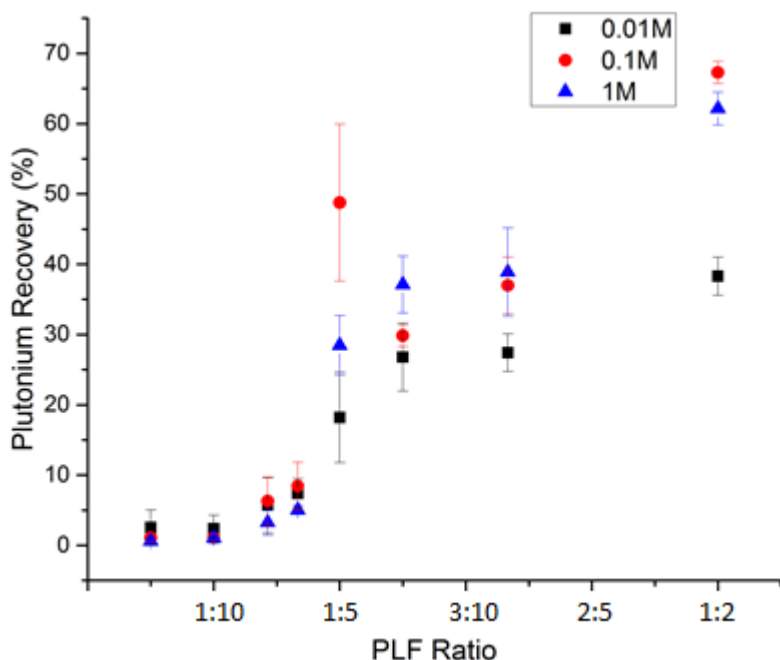
156 large amount of ligand in the PLF body is causing the PLF to be more prone to damage  
157 caused by high concentration nitric acid.



158 1:5 1:2  
159 **Fig. 4** Crown ether PLFs damaged by highly concentrated nitric acid

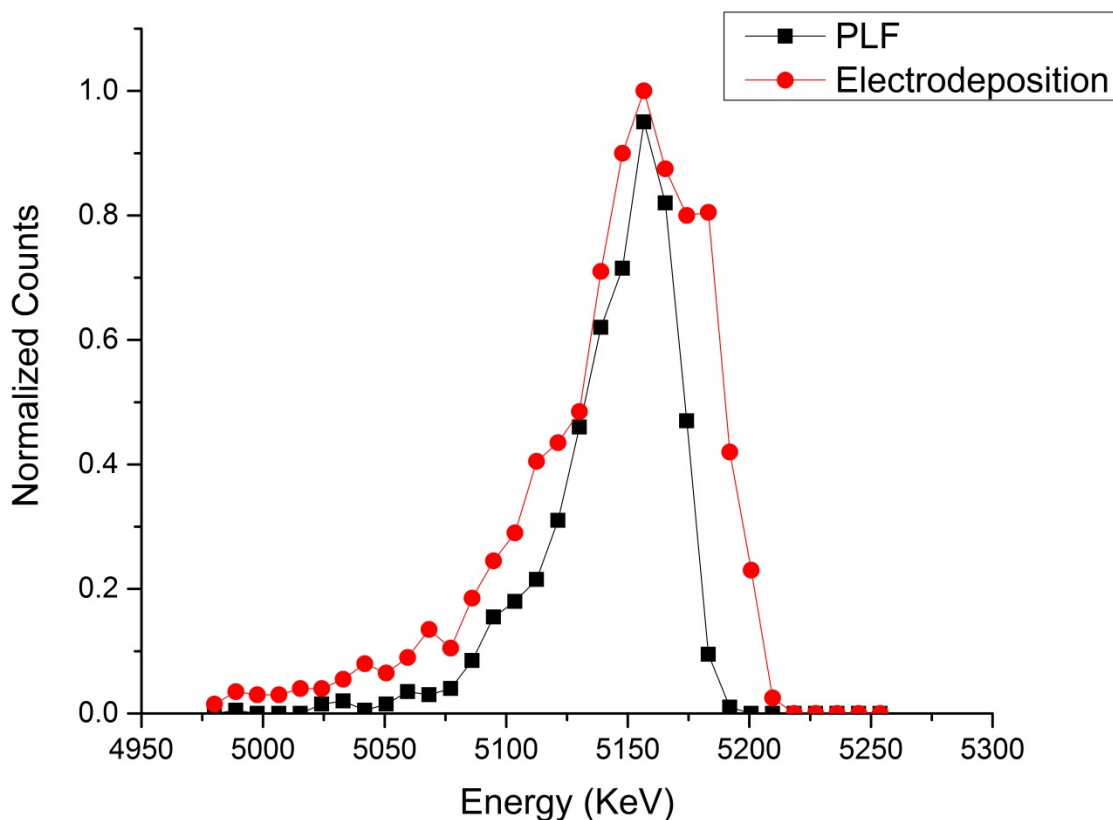
160 HDEHP PLFs were previously tested and 1:5 ratio PLF composition had given the best  
161 combination of plutonium recovery and resolution. The next closest PLF composition,  
162 1:10, was ineffective in all nitric acid concentrations. The complete drop down of  
163 recovery was unexpected and the behavior of HDEHP was further studied by preparing  
164 PLFs with smaller ratio increments over and under the 1:5 PLF. A total of four new PLF  
165 compositions were prepared: 1:3, 1:4, 1:6, and 1:7. These ratios were selected to provide  
166 finer detail between 1:2 and 1:5 and between 1:5 and 1:10 to see whether the change in  
167 plutonium extraction is a sudden or gradual change.

168 1:6 and 1:7 PLFs showed slight improvement in plutonium extraction over 1:10 or 1:20  
169 PLF in all nitric acid concentration. The plutonium recoveries were still low, below 10%,  
170 even with an increase in HDEHP ligand in PLF. Both 1:3 and 1:4 PLFs had similar  
171 spectrum tailing issue observed in 1:2 PLF. Alpha spectrum ROI was adjusted  
172 accordingly to encompass the entire counts from  $^{239}\text{Pu}$ . The long peak tailing is  
173 undesirable in alpha analysis due to possible peak convolution caused by the tail. For the  
174 case of 1:3 and 1:4 PLFs, plutonium recoveries generally fell between 1:2 and 1:5 in all  
175 nitric acid concentration except for 0.1M. In 0.1M nitric acid, 1:5 still had higher  
176 plutonium recovery than either 1:3 or 1:4 PLF. The plutonium recoveries were plotted as  
177 function of PLF ratio in Fig. 5 to better show the recovery transition as the function of  
178 PLF ratio.



**Fig. 5** Plutonium recovery by HDEHP PLF as function of PLF composition

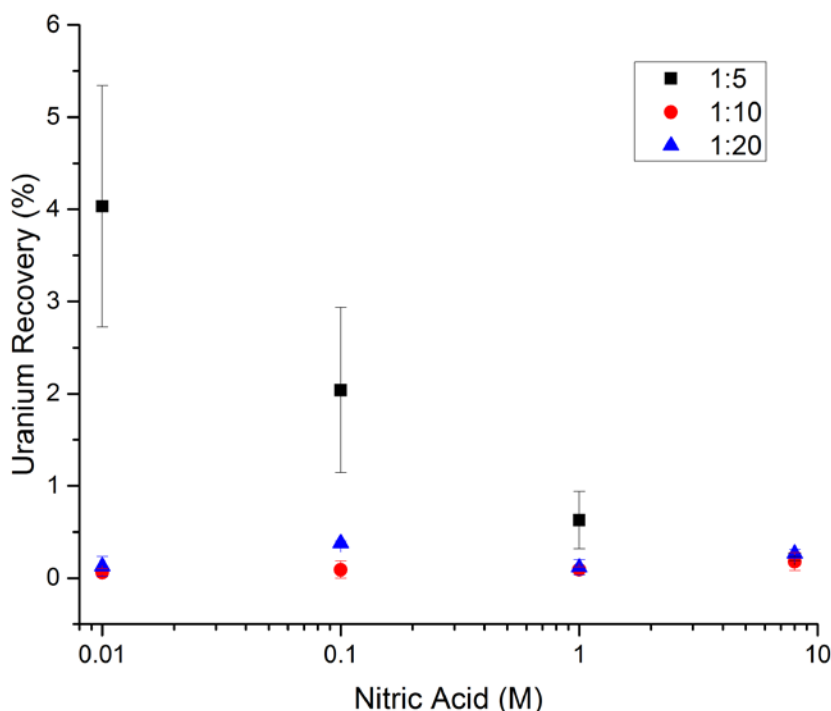
There were sudden plutonium recovery efficiency change from 1:6 and 1:5 PLF. It seems to be that 1:5 is a transitioning point from low to high recovery. This greatly suggests that ligands have to reach a certain mass compared to polymer to become available for analyte extraction. The behaviors were similar for all three nitric acid concentrations shown in Fig. 6. In 0.01M and 1M nitric acid, percent plutonium recovery reached a plateau at between 1:3 and 1:4 before achieving the highest plutonium recovery with 1:2 PLF. In 0.1M nitric acid, however, plutonium recovery spiked at 1:5 PLF then significantly decreased at 1:4 PLF. Plutonium recoveries then start to linearly increase from 1:4 to 1:2 PLF. The 1:5 PLFs consistently had large standard deviations with 0.1M nitric acid. The standard deviation could be a result of slight inconsistency in PLF composition. The 1:5 PLF is right at the transition point and slight change in ratio may dramatically change the plutonium recovery. PLF alpha spectra showed similar resolution as the samples prepared through electrodeposition method. The similarity between PLF and electrodeposition sample spectra can be also seen in a visual inspection of the plotted data. Fig. 6 was plotted with normalized count data from PLF and electrodeposited samples.



**Fig. 6** PLF and electrodeposition sample alpha spectra comparison

HDEHP was designed for an actinide group separation and also showed high affinity for uranium [12]. Since uranium alpha spectra peaks are well separated from plutonium peaks, it is possible to co-extract plutonium and uranium onto PLF then measure activities using alpha spectroscopy. PLFs were examined for uranium extraction using a natural uranium tracer. The condition tested for uranium extraction was the same as most of the plutonium experiment; 1:5, 1:10, and 1:20 H<sub>2</sub>DEH[MDP] PLFs were tested over 0.01 to 8M nitric acid solutions. 1:2 PLF was excluded from uranium study due to the sample attenuation issue observed from the plutonium samples. The uranium extraction with HDEHP PLF was ineffective in all condition tested as shown in Fig. 7. The maximum uranium recovery was only slightly higher than 4%. The ineffectiveness for uranium extraction shown by HDEHP is most likely due to the polymer support structure. HDEHP ligand has a high distribution ratio for uranium [13]. The polymer used in PLF has no direct affinity to plutonium or uranium; however, it is clearly affecting the analyte

211 extraction behavior of the ligand. In PLF, ligands were immobilized by the polystyrene  
212 and that had great effect on the analyte extraction behavior.



213  
214 **Fig. 7** Uranium recoveries by HDEHP PLF in varying nitric acid concentrations

## 215 Conclusions

216 HEH[EHP] PLF plutonium extraction was lower than H<sub>2</sub>DEH[MDP] and HDEHP PLFs.  
217 The highest recovery for HEH[EHP] was only about 25% compared to 50% and 49% for  
218 H<sub>2</sub>DEH[MDP] and HDEHP, respectively. However, HEH[EHP] was more consistent in  
219 plutonium recovery over the entire nitric concentration studied. DtBuCH<sub>18</sub>C<sub>6</sub> PLF  
220 showed no affinity to plutonium. H<sub>2</sub>DEH[MDP] and HDEHP PLFs had still shown the  
221 best plutonium recovery and alpha spectra resolutions that were consistently comparable  
222 to electrodeposited samples. HDEHP PLF was further studied for uranium recovery but  
223 showed no affinity for uranium. The PLF method greatly saved the analysis time in a  
224 laboratory setting combining column separation and electrodeposition steps into a single  
225 step. The overall analyte recoveries by PLFs were lower than typical electrodeposited  
226 samples. However, the new method has a great potential to be deployed as a screening

tool to decrease the number of samples required for more extensive analysis. The reduction in time and simplified procedure make this technique ideal for post-detonation emergency response.

Future work is planned to perform more detailed studies with respect to elimination of interference of other alpha-emitting radionuclides, such as  $^{241}\text{Am}$ , to show effectiveness of PLF in selectively extracting plutonium or uranium over other interferences.

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